

## PRENYLATED FLAVONOIDS AS EVOLUTIONARY INDICATORS IN THE GENUS *DAHLSTEDTIA*

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**Key Word Index**—*Dahlstedtia pinnata*, *D. pentaphylla*, Leguminosae, prenylated flavonoids, evolutionary indicators.

**Abstract**—Three chalcones, two  $\beta$ -hydroxychalcones, four flavanones, six flavones, four flavonols, one rotenoid and one pterocarpan were isolated from the roots of *Dahlstedtia pinnata* and *D. pentaphylla*. With the exception of the pterocarpan, all the compounds exhibit prenylation in the A ring, a characteristic of flavonoids produced by species of the Tephrosieae. Of the 21 flavonoids identified, five (2 flavanones and 3 flavones) are new as naturally occurring compounds. A neat distinction in the biosynthetic capability of the two species, leading to the production of flavanones and flavonols in *D. pentaphylla*, but not in *D. pinnata*, is observed. In this latter species, biosynthesis is totally oriented toward dehydrogenation, producing flavones. By both criteria—higher oxidation state and suppression of enzyme systems—*D. pinnata* is the more advanced species.

### INTRODUCTION

Prenylated flavonoids are characteristic constituents of a number of Leguminosae genera in the subfamily Papilionoideae, such as *Derris*, *Lonchocarpus*, *Milletia*, *Mundulea*, *Piscidia*, *Pongamia* and *Tephrosia*. Bentham [1] stressed the difficulty of neatly distinguishing these genera and this difficulty was acknowledged by most subsequent workers. Engler [2] placed them in two tribes Dalbergiae, subtribe Lonchocarpaceae; and Astragalae, subtribes Tephrosinae and Psoraleinae. Hutchinson [3] distributed them over four tribes: Milletieae, Lonchocarpeae, Tephrosieae and Psoraleae. Polhill and Geesink [4], on the other hand, united these genera into a single tribe, Tephrosieae, a decision maintained by Geesink [5], under Milletieae.

*Dahlstedtia* Malme, which has not previously been investigated chemically, belongs to this same complex. It is an exclusively Brazilian genus with only two known species: *D. pinnata* (Benth.) Malme [6] and *D. pentaphylla* (Taub.) Burk. [7]. Both have their centre of dispersion in the southern State of Santa Catarina, to which the latter species seems to be restricted, whereas *D. pinnata* can also be found further to the north, occasionally as far as Rio de Janeiro, Minas Gerais and Goiás.

In the present paper we describe the isolation and identification of 19 prenylated flavonoids from the roots of the two mentioned species, apart from two isoflavonoids (one rotenoid and one non-prenylated pterocarpan).

Only two of these components—one chalcone, **1**, and one flavone, **7**, were isolated from both species. Five are described for the first time as naturally occurring substances. This prolific presence of compounds of a peculiar type in one small genus offers an interesting overview allowing for a number of conclusions with regard to biogenetic and evolutionary aspects, based on the metabolic pathways which govern the synthesis of these secondary products.

### RESULTS AND DISCUSSION

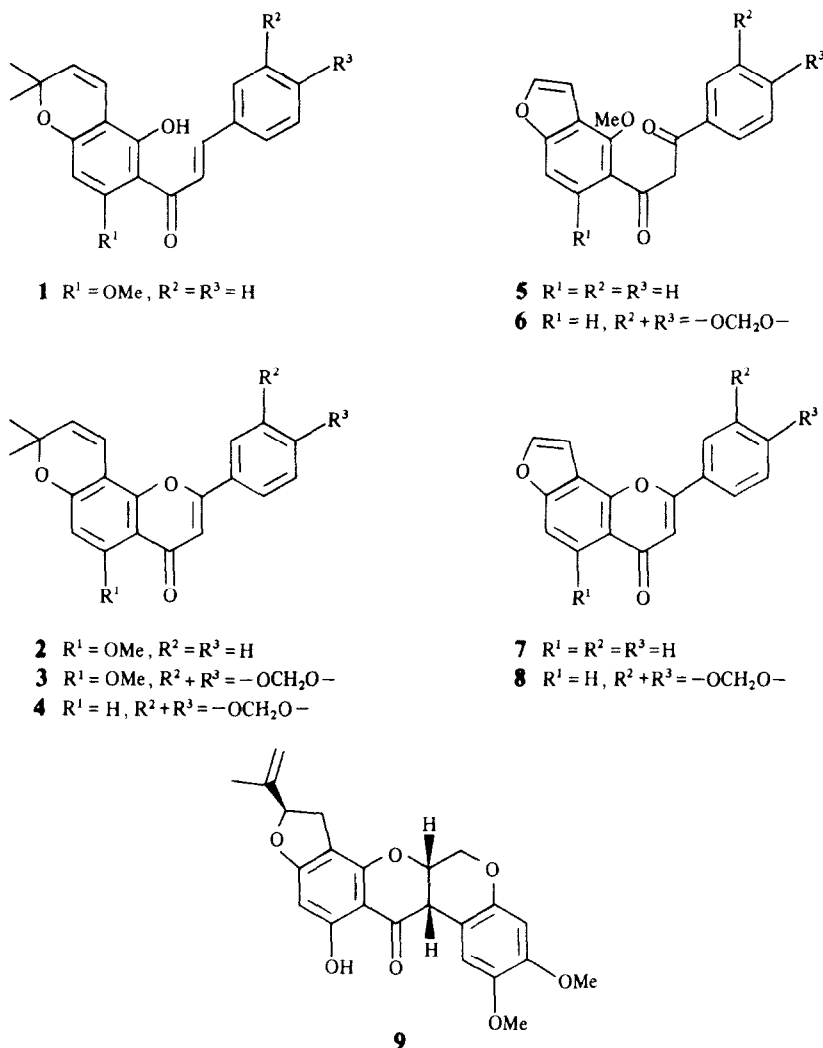
Charts 1 and 2 show the 21 identified flavonoid constituents of the two *Dahlstedtia* species. Their structures were deduced by spectral methods. Most of the compounds were known previously from plants in other genera of the tribe. Their names and the corresponding literature references are indicated in the Experimental Section. Flavones **3**, **4** and **12** and the flavanone **13** have been described as transformation products of the corresponding chalcones. Consequently, **13** was known only as the optically inactive racemate. Only flavanone **15** is new. Thus, almost all the structures, deduced from the spectral analysis, could be confirmed by comparison with physical constants and spectral data contained in the literature.

Inspection of the structures leads to a number of interesting deductions with regard to the synthetic sequences leading to the final products. It is understood, of course, that the plants produce not only those compounds which could be isolated, but all intermediates on the synthetic route as well, such as would be expected to fill in the steps in the accepted biogenetic pathways.

Comparison of the structural features with each Chart allows for the following conclusions: (i) all modifications incidental to ring A occur at least at the chalcone stage of biosynthesis. *O*-Methylation and, in the case of the re-

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Compounds 3 and 4 have not previously been described as natural products

Chart 1 Flavonoid constituents of *Dahlstedtia pinnata*

sorcinol oxydation pattern, elimination of the hydroxyl group at C-6' may happen even earlier, before cyclization, on the open polyketide chain. Prenylation occurs after cyclization, since otherwise the C<sub>5</sub> substituent would isomerize to a Δ<sup>1</sup>-isopentenyl group [8], (ii) Formation of β-hydroxychalcones (dibenzoylmethanes, e.g. 5 and 6) is conditioned to the absence of a hydroxyl group suitable for closure of the pyrone ring (elimination at C-6', O-methylation at C-2'); (iii) Where both C-2' and C-6' are oxygenated (phloroglucinol type) cyclization of the prenyl substituent toward the 'linear' disposition of the pyranochromene system (as found in many instances in *Pongamia*) rather than the 'angular' one (the only one present in *Dahlstedtia*) is also determined by the O-methylation pattern.

Altogether, one observes a neat distinction in the synthetic capability of the two *Dahlstedtia* species. Thus, *D. pentaphylla* operates the complete biogenetic sequence of flavonoid biosynthesis up to flavanones and flavonols. In *D. pinnata*, on the other hand, biosynthesis is totally oriented toward dehydrogenation, producing flavones as final products. By both criteria—higher oxydation state

and suppression of enzyme activity—*D. pinnata* is the evolutionary more advanced species.

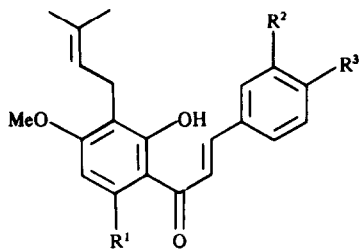
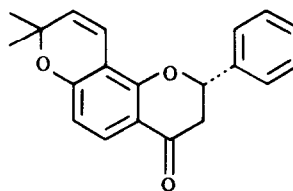
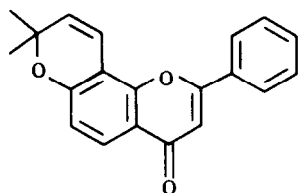
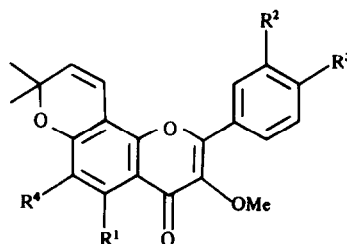
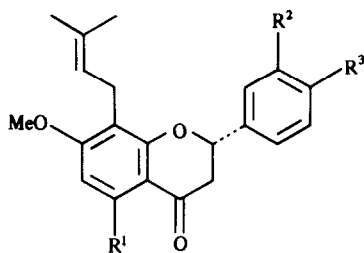
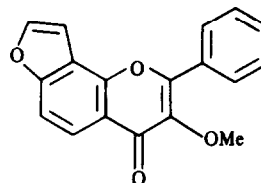
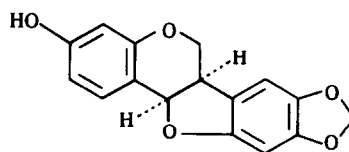
Discussion of the <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds 5 and 6 with a view on the structures involved in the respective keto-enol tautomerism in chloroform solution was the object of a previous paper [9]. The <sup>13</sup>C spectra of a larger number of flavonoids, including the compounds here described, will be presented and discussed in a forthcoming publication. An expansion of the method of reasoning here applied to the phylogenetic relationship between the two *Dahlstedtia* species to other genera of the tribe is being attempted.

#### EXPERIMENTAL

Root material of *D. pinnata* and *D. pentaphylla* was collected in the State of Santa Catarina, in the municipalities of Morretes and Rodeio, respectively. Voucher specimens are deposited at the Museu Botânico Municipal in Curitiba, Paraná.

Mps are uncorr. UV spectra were obtained in MeOH or 95% EtOH and IR spectra in KBr pellets. <sup>1</sup>H NMR spectra were recorded at 100 MHz in CDCl<sub>3</sub> with TMS as int. standard.

1 and 7 as in Chart 1

**10** R<sup>1</sup> = OMe; R<sup>2</sup> = R<sup>3</sup> = H**11** R<sup>1</sup> = OMe, R<sup>2</sup> + R<sup>3</sup> = -OCH<sub>2</sub>O-**16****12****17** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H**18** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H, R<sup>4</sup> = OMe**19** R<sup>1</sup> = R<sup>4</sup> = H; R<sup>2</sup> + R<sup>3</sup> = -OCH<sub>2</sub>O-**13** R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H**14** R<sup>1</sup> = OMe, R<sup>2</sup> = R<sup>3</sup> = H**15** R<sup>1</sup> = H, R<sup>2</sup> + R<sup>3</sup> = -OCH<sub>2</sub>O-**20****21**

Flavanone **15** is new in the literature; flavone **12** and flavanone **13** have not previously been described as natural products, the latter being formerly known only in the racemic form.

Chart 2 Flavonoid constituents of *Dahlstedtia pentaphylla*

chemical shifts are reported in  $\delta$  (ppm) units MS were recorded on a Varian Micromass MM 12F instrument at 70 eV Silicic acid and silica-gel were used for CC, while silica-gel GF and PF<sub>254</sub> were used for TLC Spots were visualized by exposing the plates to I<sub>2</sub> vapour, by spraying with CeSO<sub>4</sub> in 2N H<sub>2</sub>SO<sub>4</sub> and by inspection under UV light (254 and 366 nm). Elution of the columns was started with petrol (bp 40–80°) and proceeded with solvent mixtures of increasing polarity.

**Extraction** Ground roots were exhaustively percolated first with petrol, then with Et<sub>2</sub>O The extractives were redissolved in petrol and chromatographed as indicated above Of the nine

flavonoids isolated from *D. pinnata*, eight were present in both extracts, one (**9**) was present in the petrol extract only. Of the 14 flavonoids isolated from *D. pentaphylla*, **11** was present in the petrol extract exclusively, five (**12**, **14**, **16**, **19** and **21**) were present only in the Et<sub>2</sub>O extract, and the remaining eight, in both Below, the compounds are listed in the order of their elution Our data not previously published are reported here.

*2-Hydroxy-6'-methoxy-2'', 2''-dimethylpyrano (5'', 6''- 3', 4') chalcone (1, pongachalcone I).* Eluted with hexane-EtOAc 99/1, orange-red crystals from hexane, mp 105–108° (lit. [10] 107–108°) UV  $\lambda_{\max}^{\text{MeOH}}$  nm (log  $\epsilon$ ) 232 (4.29), 304 (4.36), 358

(430) UV  $\lambda_{\text{max}}^{\text{MeOH}+\text{AlCl}_3}$  nm (log  $\epsilon$ ) 228 (426), 306 (424), 390 (433) MS  $m/z$  [M<sup>+</sup>]

2-Methoxy-2',3',3',4'-furanodibenzoylmethane [=2-methoxy-2',3',3',4'-furan- $\beta$ -hydroxychalcone] (**5**, pongamol) Eluted with hexane-EtOAc (98/2), red crystals from hexane-EtOAc (3/1), mp 134–137° (lit [11] 128–129°) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm (log  $\epsilon$ ) 221 (418), 239 (429), 350 (424) MS  $m/z$  (rel int.) 294 [M<sup>+</sup>], (10), 263 (100), 175 (68), 160 (20), 105 (28), 77 (32)

2-Methoxy-3',4'-methyleneedioxy-2',3',3',4'-furanodibenzoylmethane [=2-methoxy-3',4'-methyleneedioxy-2',3',3',4'-furan- $\beta$ -hydroxychalcone] (**6**, glabra-I, ovalitenone) Eluted with hexane-EtOAc (95/5), greenish-yellow crystals, mp 120–123 (lit [12] 123–126°) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm (log  $\epsilon$ ) 221 (406), 240 (424), 367 (419) UV  $\lambda_{\text{max}}^{\text{EtOH}+\text{NaOH}}$  nm (log  $\epsilon$ ) 221 (450), 350 (425) MS  $m/z$  (rel int.) 338 [M<sup>+</sup>] (18), 307 (100), 175 (76), 160 (21), 149 (41), 121 (13)

(2',3',7,8)-Furanoflavone (**7**, lanceolatin B) Eluted with hexane-EtOAc (9/1), pale yellow crystals, mp 134–137° (lit [13] 138°) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm (log  $\epsilon$ ) 224 (430), 264 (433), 297 (421) MS  $m/z$  (rel int.) 262 [M<sup>+</sup>] (61), 234 (5), 160 (100), 132 (12), 117 (9), 104 (7) <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.88 (1H, s, H-3), 7.20 (1H, d,  $J$  = 2.0 Hz, H- $\beta$ ), 7.50–7.62 (4H, m, H-3', H-4', H-5', H-6), 7.80 (1H, d,  $J$  = 2.0 Hz, H- $\alpha$ ), 7.90–8.02 (2H, m, H-2', H-6'), 8.16 (1H, d,  $J$  = 9.0 Hz, H-5)

3',4'-Methyleneedioxy-2',3',7,8)-furanoflavone (**8**, pongaglabrone) Eluted with hexane-EtOAc (9/1), colourless crystals, mp 228–230° (lit [14] 228–229°) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm (log  $\epsilon$ ) 223 (447), 249 (452), 329 (432) MS  $m/z$  (rel int.) 306 [M<sup>+</sup>] (100), 278 (7), 160 (68), 146 (94), 132 (11), 104 (5) <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6.14 (2H, s, O-CH<sub>2</sub>-O), 6.80 (1H, s, H-3), 7.0 (1H,  $J$  = 8.0 Hz, H-5'), 7.20 (1H, d,  $J$  = 2.0 Hz, H- $\beta$ ), 7.44 (1H, d,  $J$  = 2.0 Hz, H-2'), 7.59 (2H, dd,  $J$  = 8.0 and 2.0 Hz, H-6, H-6'), 7.82 (1H, d,  $J$  = 2.0 Hz, H- $\alpha$ ), 8.22 (1H,  $J$  = 8.0 Hz, H-5)

3',4'-Methyleneedioxy-2',2''-dimethylpyrano-(5'',6'',7,8)-flavone (**4**) Eluted with hexane-EtOAc (9/1), yellow crystals, mp 232–234° (lit [15] 233°) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm (log  $\epsilon$ ) 237 (438), 270 (412), 339 (414) MS  $m/z$  (rel int.) 384 [M<sup>+</sup>] (15), 333 (100), 187 (47) <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.52 (6H, s, gem-dimethyl), 5.73 (1H, d,  $J$  = 9.0 Hz, H-3''), 6.05 (2H, s, O-CH<sub>2</sub>-O), 6.60 (1H, s, H-3), 6.82 (1H, d,  $J$  = 8.0 Hz, H-6), 6.87 (1H, d,  $J$  = 9.0 Hz, H-4''), 6.91 (1H, d,  $J$  = 8.0 Hz, H-5'), 7.29 (1H, d,  $J$  = 2.0 Hz, H-2'), 7.43 (1H, dd,  $J$  = 8.0 and 2.0 Hz, H-6'), 7.95 (1H, d,  $J$  = 8.0 Hz, H-5)

6a,12a,4',5'-Tetrahydro-11-hydroxy-2,3-dimethoxy-5'-isopropenylfuran-(3',2',8,9)-6H-rotaxen-12-one (**9**, sumatrol) Eluted with hexane-EtOAc (9/1), colourless crystals, mp 192–194° (lit [16] 194–195°), [ $\alpha$ ]<sub>D</sub><sup>25</sup> –21.7 (CHCl<sub>3</sub>, c0.77), –187° (C<sub>6</sub>H<sub>6</sub>, c0.5)

5-Methoxy-2'',2''-dimethylpyrano-(5'',6'',7,8)-flavone (**2**, isopongaflavone) Eluted with hexane-EtOAc (1/1), pale yellow crystals, mp 214–216° (lit [17] 214–216°) MS  $m/z$  334 [M<sup>+</sup>]

5-Methoxy-3',4'-methyleneedioxy-2'',2''-dimethylpyrano-(5'',6'',7,8)-flavone (**3**) Eluted with hexane-EtOAc (3/7), pale yellow crystals, mp 242–244° (lit [18] 242–244°) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm (log  $\epsilon$ ) 236 (448), 276 (438), 331 (418) MS  $m/z$  (rel int.) 378 [M<sup>+</sup>] (53), 363 (100), 217 (70)

2'-Hydroxy-4,6'-dimethoxy-3'- $\gamma$ , $\gamma$ -dimethylallylchalcone (**10**, ovalchalcone) Eluted with hexane-CHCl<sub>3</sub> (8/2), orange crystals from EtOH, mp 126–128° (lit [19] 123–124°)

(2S)-7-Methoxy-8- $\gamma$ , $\gamma$ -dimethylallylflavanone (**13**, (–)-isoderrien A) Eluted with hexane-CHCl<sub>3</sub> (7/3) Colourless crystals from EtOH, mp 103–104° (lit for the racemic compound 123° [20]) Anal C 77.94, H 6.89 Calc for C<sub>21</sub>H<sub>22</sub>O<sub>3</sub> C 78.23, H 6.88 [ $\alpha$ ]<sub>D</sub><sup>28</sup> –91.1° (CHCl<sub>3</sub>, c1.0) UV  $\lambda_{\text{max}}^{\text{EtOH}}$  nm (log  $\epsilon$ ) 220 (417), 237 (380, sh), 286 (382), 312 (340, sh) <sup>1</sup>H NMR  $\delta$  1.68 (6H, s, gem-dimethyl), 2.72–3.18 (2H, m, H-3), 3.36 (2H, dl,  $J$  = 7 Hz, –CH<sub>2</sub>–CH=), 3.92 (3H, s, 7-OMe), 5.20 (1H, *tl*,  $J$  = 7 Hz,

–CH<sub>2</sub>–CH=), 5.46 (1H, *dd*,  $J$  = 11 and 5 Hz, H-2), 6.63 (1H, *d*,  $J$  = 9 Hz, H-6), 7.38–7.48 (5H, *m*, C<sub>6</sub>H<sub>5</sub>), 7.83 (1H, *d*,  $J$  = 9 Hz, H-5) MS  $m/z$  322 [M<sup>+</sup>] (45), 307 (22), 279 (44), 267 (16), 218 (90), 203 (58), 190 (100), 175 (94), 163 (50), 131 (21), 104 (10), 103 (18) CD (MeOH, c0.022 g/l) [ $\theta$ ]<sub>352</sub> = 0, [ $\theta$ ]<sub>333</sub> = 23426, [ $\theta$ ]<sub>319</sub> = 0, [ $\theta$ ]<sub>292</sub> = –32211

2'-Hydroxy-4,6'-dimethoxy-3'- $\gamma$ , $\gamma$ -dimethylallyl-3,4-methylene-dioxychalcone (**11**, ovalchalcone A) Eluted with hexane-CHCl<sub>3</sub> (7/3), orange crystals from EtOH, mp 158–162 (lit [21] 158°) MS  $m/z$  (rel int.) 396 [M<sup>+</sup>] (87), 381 (19), 353 (57), 341 (25), 275 (4), 248 (15), 233 (58), 219 (12), 205 (33), 193 (66), 191 (30), 175 (100), 165 (6), 147 (12)

(2S)-7-Methoxy-8- $\gamma$ , $\gamma$ -dimethylallyl-3,4'-methyleneedioxyflavanone (**15**) Eluted with hexane-CHCl<sub>3</sub> (6/4), colourless crystals from EtOH, mp 120–122 Anal C 71.95 H 5.9 Calc for C<sub>22</sub>H<sub>22</sub>O<sub>5</sub> C 72.11, H 6.05 [ $\alpha$ ]<sub>D</sub><sup>38</sup> –80.3 (CHCl<sub>3</sub>, c1.0) <sup>1</sup>H NMR  $\delta$  1.68 (6H, *sl* gem-dimethyl), 2.66–3.14 (2H, *m*, H-3), 3.35 (2H, *dl*,  $J$  = 7 Hz, –CH<sub>2</sub>–CH=), 3.91 (3H, s, 7-OMe), 5.18 (1H, *tl*,  $J$  = 7 Hz, –CH<sub>2</sub>–CH=), 5.35 (1H, *dd*,  $J$  = 11 and 5 Hz, H-2), 5.99 (2H, s, O-CH<sub>2</sub>-O), 6.62 (1H, *d*,  $J$  = 9 Hz, H-6), 6.84–7.00 (3H, *m*, H-2, H-5', H-6'), 7.82 (1H, *d*,  $J$  = 9 Hz, H-5) MS  $m/z$  (rel int.) 366 [M<sup>+</sup>] (100), 351 (12), 323 (88), 311 (31), 218 (40), 203 (36), 190 (60), 175 (73), 163 (62), 148 (65), 147 (29), 135 (14) CD (MeOH, c0.028 g/l) [ $\theta$ ]<sub>334</sub> = 24836, [ $\theta$ ]<sub>320</sub> = 0, [ $\theta$ ]<sub>296</sub> = –45752

3-Methoxy-2'',3''-furanoflavone (**20**, karanjum) Eluted with hexane-CHCl<sub>3</sub> (1/1), colourless crystals, mp 161–163° (lit [22] 161°)

3-Methoxy-2'',2''-dimethylpyrano-(5'',6'',7,8)-flavone (**17**, pongaflavone, karanjachromene) Eluted with hexane-CHCl<sub>3</sub> (1/1), colourless crystals, mp 148–150 (lit [22] 149°)

3,6-Dimethoxy-2'',2''-dimethylpyrano-(5'',6'',7,8)-flavone (**18**) Eluted with hexane-CHCl<sub>3</sub> (25/75), colourless crystals from EtOH, mp 201–203 (lit [23,24] 203–205°)

(2S)-2'',2''-Dimethylpyrano-(5'',6'',7,8)-flavanone (**16**, (–)-isolonchocarpine) Eluted from Et<sub>2</sub>O extract with hexane-CHCl<sub>3</sub> (6/4), colourless crystals, mp 114–116 (lit [25,26] 117–118°) CD (MeOH, c0.0325 g/l) [ $\theta$ ]<sub>355</sub> = 0, [ $\theta$ ]<sub>330</sub> = 13207, [ $\theta$ ]<sub>310</sub> = 0, [ $\theta$ ]<sub>305</sub> = –37736

3-Methoxy-2'',2''-dimethylpyrano-(5'',6'',7,8)-3',4'-methylene-dioxyflavone (**19**, pongachromene) Eluted from Et<sub>2</sub>O extract with hexane-EtOAc (9/1), light yellow crystals from EtOH, mp 198–200 (lit [27] 195–196°) MS  $m/z$  (rel int.) 378 [M<sup>+</sup>] (79), 377 (70), 363 (100), 187 (48), 159 (12), 149 (30)

2'',2''-Dimethylpyrano-(5'',6'',7,8)-flavone (**12**) Eluted from Et<sub>2</sub>O extract with hexane-EtOAc (8/2) Light yellow crystals from EtOH, mp 136–140° (lit [28] 142°)

(6aR, 11aR)-3-Hydroxy-8,9-methyleneoxypterocarpan (**21**, maackian, demethylpterocarpan) Eluted from Et<sub>2</sub>O extract with hexane-EtOAc (85/15) Yellow amorphous solid Identification by spectral data (for mass spectrum see [29]) and acetylation (see below) <sup>1</sup>H NMR  $\delta$  3.34–3.80 (2H, *m*, H-6a and H-6 axial), 4.13–4.30 (1H, *m*, H-6 equatorial), 5.50 (1H, *d*,  $J$  = 7 Hz, H-11a), 5.92 (2H, *m*, –O-CH<sub>2</sub>-O–), 6.47 (1H, s, H-10), 6.52 (1H, *d*,  $J$  = 3 Hz, H-4), 6.67 (1H, *dd*,  $J$  = 8 and 3 Hz, H-2), 6.74 (1H, s, H-7), 7.38 (1H, *d*,  $J$  = 8 Hz, H-1)

(2S)-5,7-Dimethoxy-8- $\gamma$ , $\gamma$ -dimethylallylflavanone (**14**) Eluted from Et<sub>2</sub>O extract with hexane EtOAc (7/3) Colourless crystals from CHCl<sub>3</sub>-Me<sub>2</sub>O, mp 97–100 (lit [30] 98°) [ $\alpha$ ]<sub>D</sub> –33° (CHCl<sub>3</sub>, c1.0) CD (MeOH, c0.0365 g/l) [ $\theta$ ]<sub>359</sub> = 0, [ $\theta$ ]<sub>333</sub> = 15384, [ $\theta$ ]<sub>310</sub> = 0, [ $\theta$ ]<sub>280</sub> = –47115

Acetylation of **21** (6aR, 11aR)-3-acetoxy-8,9-methyleneoxypterocarpan The material was acetylated with Ac<sub>2</sub>O in pyridine in the usual way The product was recrystallized  $\times$ 2 from EtOAc Colourless crystals, mp 177–180 (lit [31,32] 178°) MS  $m/z$  (rel int.) 326 [M<sup>+</sup>] (39), 284 (100), 283 (17), 175 (7), 162 (13), 151

(7), 149 (5), 147 (6), 134 (12) ORD (MeOH,  $c$  0.042 g/l)  $[\theta]_{350} = -776$ ,  $[\theta]_{320} = 3381$ ,  $[\theta]_{312} = 0$ ,  $[\theta]_{285} = -24062$ ,  $[\theta]_{273} = -17852$ ,  $[\theta]_{244} = -27943$

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